⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 043 512**
A1

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: 81104934.5

㉒ Date of filing: 25.06.81

(51) Int. Cl.^{3}: **C 08 L 27/06**, C 08 L 25/16

㉚ Priority: 28.06.80 JP 88398/80

㊸ Date of publication of application: 13.01.82
Bulletin 82/2

(84) Designated Contracting States: BE DE FR GB IT NL

(71) Applicant: Kanegafuchi Kagaku Kogyo Kabushiki Kaisha, 2-4, 3-chome, Nakanoshima Kita-ku, Osaka-shi Osaka-fu (JP)

(72) Inventor: Mathumoto, Sigemi, 329, Nagao, Amida-cho, Takasago-shi Hyogo-ken (JP)
Inventor: Kubota, Hidetaka, 1-49-305, 4-chome Shinryodai Tarumi-ku, Kobe-shi Hyogo-ken (JP)
Inventor: Nagoshi, Fumiya, 9-36, 9-chome Nishimaiko Tarumi-ku, Kobe-shi Hyogo-ken (JP)

(74) Representative: Vossius.Vossius.Tauchner.Heunemann.Rauh, Siebertstrasse 4 P.O. Box 86 07 67, D-8000 München 86 (DE)

(54) Thermoplastic resin compositions.

(57) Thermoplastic resin compositions which comprise 20–70 parts by weight of a polyvinyl chloride resin and 80–30 parts by weight of a mixed composition of the following copolymers (A) and (B) in the following ratio:

(A) 90–50% by weight of a copolymer which comprises 65–90 parts by weight of α-methylstyrene with 35–10 parts by weight of acrylonitrile and 0–5 parts by weight of at least one copolymerizable vinyl monomer and contains 30 parts by weight or more of a component having an α-methylstyrene content of 82% by weight or higher; and

(B) 10–50% by weight of a graft copolymer obtained by reacting 35–80% by weight of a conjugated diene rubber and 65–20% by weight of a monomer comprising an aromatic monovinyl compound, an unsaturated nitrile compound or an alkyl methacrylate.

These compositions have greatly improved heat resistance, especially resistance to heat distortion, and impact resistance over those of polyvinyl chloride resins.

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BACKGROUND OF THE INVENTION

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1. Field of the Invention

This invention relates to thermoplastic resin compositions having good heat resistance or a combination of good heat resistance and impact resistance. More particualrly, it relates to resin compositions which comprise a polyvinyl chloride resin and a mixture of a copolymer (A) containing α-methylstyrene as a main component and a graft copolymer (B) obtained by graft polymerization of a conjugated diene rubber with an aromatic vinyl compound and an unsaturated nitrile compound or an alkyl methacrylate, and it relates to thermoplastic resin compositions having greatly improved resistance to heat distortion and impact resistance over those of polyvinyl chloride resins.

2. Description of the Prior Art

Polyvinyl chloride resins have excellent mechanical characteristics and electrical characteristics and possess characteristic physical properties such as transparency, flame retardation, etc., as well as versatile working characteristics, and thus they are extensively employed as useful plastic materials in various fields of applications. However, the resins of this type have a thermal distortion temperature of 65 - 70°C, and therefore their use is limited where the articles are subjected to high temperature environments, for example, pipes for hot water, automobile interior parts etc. where the indoor temperature may become very high.

Heretofore, there have been provided various methods to overcome this disadvantage of the polyvinyl chloride resins, e.g., those involving incorporating an AS (acrylonitrile - styrene) resin, an ABS (acrylonitrile - butadiene - styrene) resin and an MBS (methyl methacrylate - butadiene - styrene) resin, respectively, to polyvinyl chloride resins. There has also been proposed a method which comprises introducing α-methylstyrene monomer as one component of these resins in order to further enhance the effect of improving heat resistance. For example, Japanese Patent Publication No. 24867/1970 describes how a composition having high heat resistance is obtained by blending a polyvinyl chloride resin with a copolymer of methyl methacrylate, acrylonitrile, styrene and α-methylstyrene and a butadiene containing polymer. However, the amount of α-methylstyrene in the copolymer is at best merely 45% by weight and heat resistance is not adequate. Further, Japanese Patent Publication No. 18101/1973 describes a method which comprises incorporating a resin (A), obtained by copolymerizing a monomer mixture consisting of 5 - 50% of methyl methacrylate, 3 - 30% of acrylonitrile and 30 - 80% of α-methylstyrene together with a butadiene containing graft polymer, into a polyvinyl chloride resin. However, it can be estimated from the reactivity on copolymerization that by this method it is practically impossible to make the α-methylstyrene content in this copolymer (A) 70% by weight or higher even locally.

We have discovered that the high heat resistance which has not been achieved in the above-described prior art techniques can be obtained by incorporating a copolymer (A), which is a copolymer comprising 65 - 90 parts by weight of α-methylstyrene with 35 - 10 parts by weight of acrylonitrile and 0 - 5 parts by weight of at least one copolymerizable vinyl monomer and containing 30 parts by weight or more of a component having an α-methylstyrene content of 82% by weight or higher, and a graft copolymer (B) obtained by reacting 35 - 80% by weight of a conjugated diene rubber with 65 - 20% by weight of a monomer comprising an aromatic monovinyl compound and an unsaturated nitrile compound or an alkyl methacrylate, into a polyvinyl chloride resin, and thus accomplished this invention.

SUMMARY OF THE INVENTION

Accordingly, this invention provides a thermoplastic resin composition which comprises 20 - 70 parts by weight of a polyvinyl chloride resin and 80 - 30 parts by weight of a mixed composition of the following copolymers (A) and (B) in the following mixing ratio:

(A) 90 - 50% by weight of a copolymer which comprises 65 - 90 parts by weight of α-methylstyrene with 35 - 10 parts by weight of acrylonitrile and 0 - 5 parts by weight of at least one copolymerizable vinyl monomer and contains 30 parts by weight or more of a component having an α-methylstyrene content of 82% by weight or higher; and

(B) 10 - 50% by weight of a graft copolymer obtained by reacting 35 - 80% by weight of a conjugated diene rubber and 65 - 20% by weight of a monomer or monomers comprising an aromatic monovinyl compound, an unsaturated nitrile compound or an alkyl methacrylate.

DESCRIPTION OF THE PREFERRED EMBODIMENT

One component of the compositions of this invention is an α-methylstyrene containing copolymer (A). Said copolymer is used to impart heat resistance to the intended composition and may be obtained as follows: α-Methylstyrene monomer is first changed into a reaction system for emulsion polymerization and, after making the system fully emulsified, acrylonitrile is continuously added dropwise with a very small amount each time, while in the polymerization system the proportion of the α-methylstyrene monomer and the acrylonitirle monomer is always maintained at such great excess of α-methylstyrene as a weight ratio of 90/10 or higher, more preferably 95/5 or higher. Thereby the desired copolymer is obtained. In this case, α-methylstyrene to be charged first is at least 65 parts by weight and up to 90 parts by weight. With an amount of less than 65 parts by weight, the effect is inadequate for improving heat resistance, while with an amount of more than 90 parts by weight, compatibility with polyvinyl chloride resins is lowered. The amount of acrylonitrile to be added dropwise continuously is at least 10 parts by weight and up to 35 parts by weight. With an amount of less than 10 parts by weight, the percent conversion to polymer is reduced, while with an amount of more than 35 parts by weight, the resulting copolymer tends to color on heating and also brings about coloration when mixed with a polyvinyl chloride resin. The α-methylstyrene monomer to be charged first may contain up to 10% by weight based on the α-methylstyrene monomer of an unsaturated nitrile compound, lower alkyl esters of methacylic acid and acrylic acid and the like. The acrylonitrile monomer to be continuously added dropwise may contain up to 15% by weight based on the acrylonitrile monomer of an aromatic monovinyl compound, an α-substituted type monovinyl aromatic compound, lower alkyl esters of methacrylic acid and acrylic acid and the like. As a third component other than α-methylstyrene and acrylonitrile, it is possible to employ up to 5 parts by weight of the above-mentioned vinyl monomer substantially without adversely affecting heat resistance or impact resistance, but when it is incorporated in an amount beyond the above range, the heat resistance of the resulting copolymer is lowered . Therefore, this is not desirable.

Another component of the compositions according to this invention is a graft copolymer (B) utilizing a conjugated diene rubber. Said copolymer is employed to impart impact resistance to the subject composition. The composition of said copolymer is such that the conjugated diene rubber comprises 35 - 80% by weight and the total of the aromatic monovinyl compound and the unsaturated nitrile compound or the alkyl methacrylate comprises 65 - 20% by weight, and it is preferred that the proportion of the alkyl methacrylate is 85 - 20 : 15 - 80 on the weight methacrylic acid alkyl ester is 85 - 20 : 15 - 80 on the weight basis. The reason is that with the amount of the conjugated diene rubber of less than 35% by weight, it is difficult to obtain the desired impact resistance. On the other hand, if the amount exceeds 80% by weight, compatibility with polyvinyl chloride resins is inadequate and thus it is difficult to obtain a uniform molded product. A further reason is that with the amount of the conjugated diene rubber in excess, the effect of improved heat resistance is reduced. Examples of the conjugated diene rubber to be used in said graft copolymer (B) include polybutadiene, polyisoprene, and butadiene - styrene copolymers, without being restricted thereto. Examples of the monovinyl aromatic compound include, in addition to styrene, α-methylstyrene, chlorostyrene, and t-butylstyrene. Examples of the unsaturated nitrile compound include acrylonitrile as well as methacrylonitrile. Examples of the alkyl methacrylate include methyl methacrylate, ethyl methacrylate.

The above-mentioned copolymer (A) and graft copolymer (B) may preferably be obtained by emulsion polymerization, but the type of polymerization is not limited to emulsion polymerization. Emulsion polymerization may be carried out in a conventional manner. For example, the above-mentioned monomer mixture may be reacted in the presence of a free-radical initiator in an aqueous dispersion. As the free-radical initiator, there may be mentioned peroxides such as potassium persulfate, ammonium persulfate, cumene hydroperoxide etc. In addition, other additives, e.g. a polymerization co-catalyst, a chain transfer agent, an emulsifier, which have heretofore been conventionally employed in emulsion polymerization may be appropriately chosen and used.

The heat resistance and impact resistance of the products molded in the compositions according to this invention can vary depending not only on the compositions of the copolymer (A) and the graft copolymer (B) respectively but also on the mixing ratio thereof, as well as the mixing ratio of those with the polyvinyl chloride resin. Therefore, the mixing ratios may be selected according to the desired heat resistance and impact resistance of the molded articles.

For obtaining the intended heat resistant resin composition according to this invention, the total amount of the copolymer (A) and the graft copolymer (B) is suitably 30 - 80 parts by weight, more preferably 30 - 70 parts by weight, in the total composition resulting from the incorporation thereof in a polyvinyl chloride resin. An amount of less than 30 parts by weight is inadequate for improving the heat resistance of the polyvinyl chloride resin, while with an amount of more than 80 parts by weight, although satisfactory heat resistance is imparted the working temperature becomes higher, which induces coloration of the polyvinyl chloride resin due to heat. This is not desirable. In order to successfully achieve this invention, the mixing ratio on the weight basis of the copolymer (A) and the graft copolymer (B) is preferably 90/10 - 50/50, more preferably 80/20 - 60/40. Where the copolymer exceeds 90% by weight, the impact resistance is lowered, although the heat resistance of the polyvinyl chloride resin is effectively improved. On the other hand, with an amount of less than 50% by weight, the effect of improving the heat resistance is small and on the other hand results in a great reduction in tensile strength. Mixing of the copolymer (A) and the graft copolymer (B) may be effected in a conventional manner.

When the compositions of this invention are subjected to working, commonly employed heat stabilizers, lubricants, pigments, fillers etc. are used as required. Specifically as heat stabilizer there may be employed, for example, organic tin based stabilizers such as organic tin maleates, organic tin laurates, organic tin mercaptides etc., lead salt based stabilizers such as white lead, tribasic lead sulfate, dibasic lead phosphite, dibasic lead phthalate, tribasic lead maleate, lead silicate and its silica gel co-precipitate etc., or metal soap stabilizers, e.g. lead, cadium, barium, zinc, calcium salts of higher fatty acids. It is also possible to use, in combination with the above, epoxy compounds such as epoxylated soybean oil, epoxylated linseed oil, and organic phosphite compounds such as triphenyl phosphite and trinonylphenyl phosphite. As lubricant, there may be employed saturated fatty acids such as stearic acid, palmitic acid and ester compounds thereof, natural waxes such as carnauba wax, candelilla wax, synthesized waxes such as ethylene bisstearylamide, polyethylene oxide, low molecular weight polyethylene, or liquid paraffin. Further as fillers, calcium carbonate, clay, silica, talc, carbon black etc. as well as flame retarders such as antimony trioxide, metastannic acid etc. may be added as required. Still further, it is also possible to use a small amount of a plasticizer such as phthalic acid esters, adipic acid esters, sebacic acid esters, phosphoric acid esters or polyesters.

This invention is more particularly described by the following examples, in which all the "parts" mean "parts by weight".

Examples and Comparative Examples

1) Production of Copolymers (A)

The following materials were charged into a reactor equipped with a stirrer.

Water	250 parts
Sodium laurate	3 parts
Sodium formaldehyde sulfoxylate	0.4 part
Ferrous sulfate	0.0025 part
Disodium ethylenediaminetetraacetate	0.01 part

After flushing with purified nitrogen and subsequent heating with stirring at 60°C in a nitrogen stream, the monomer mixture (I) indicated in Table 1 was charged. After fully emulsifying and mixing the system, the monomer mixture (II) indicated in Table 1 was continuously added dropwise. On completion of this addition, stirring was further continued at 60°C, and the polymerization was terminated. The latex in the course of the reaction was taken as samples, and the composition was analyzed and the conversion to polymer measured.

The percent conversion to polymer of the thus obtained copolymer and its composition in the course of the reaction are given in Table 1. The copolymers of this invention, as those indicated by A-1 to A-6 in Table 1, contain therein a copolymer containing 82% by weight more of α-methylstyrene. On the other hand, the case where the amount of α-methylstyrene to be charged first was 95 parts by weight was given as Comparative Example A-7, in which the conversion to polymer dropped remarkably and therefore further investigation was stopped. In the rest of the comparative examples, polymerization was effected either by charging 60 parts by weight of α-methylstyrene first or continuously adding dropwise a uniform mixture of α-methylstyrene and acrylonitrile from the start. In either case, it was difficult to make the α-methylstyrene content 82% by weight or higher even locally, and it was believed that a 1 : 1 alternative copolymer of α-methylstyrene - acrylonitrile or α-methylstyrene - methyl methacrylate comprised the greater part.

Table 1

No.	Example						Comparative Example			
	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10
Monomer Mixture (I)										
α-Methylstyrene (pts)	80	75	70	75	70	75	95	60	-	-
Acrylonitrile (pts)	-	-	-	-	5	-	-	-	-	-
t-Dodecylmercaptan (pts)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	-	-
Monomer Mixture (II)										
Acrylonitrile (pts)	20	25	30	22	22	22	5	40	30	20
α-Methylstyrene (pts)	-	-	-	3	3	-	-	-	70	70
Methyl methacrylate (pts)	-	-	-	-	-	3	-	-	-	10
Cumene hydroperoxide (pts)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
t-Dodecylmercaptan (pts)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
α-Methylstyrene Content at a Polymer Yield of 40 - 50 pts. (%)*	83	82	82	82	82	82	84	78	68	65
Final Conversion to Polymer (%)	96	97	96	97	97	97	29	92	96	93

* Calculated from the elemental analysis of the polymer.

2) Production of Graft Copolymers (B)

The following materials were charged into a reactor equipped with a stirrer.

Water	250 parts
Sodium formaldehyde sulfoxylate	0.2 part
Ferrous sulfate	0.0025 part
Disodium ethylenediaminetetraacetate	0.01 part
Polybutadiene	60 parts

After flushing with purified nitrogen and subsequent heating with stirring at 60°C in a nitrogen stream, 40 parts of the following monomer mixture was continuously added dropwise together with 0.3 part of cumene hydroperoxide. On completion of the addition, stirring was further continued at 60°C and then the polymerization was terminated.

B-1: 12 parts of acrylonitirle and 28 parts of styrene

B-2: 5 parts of acrylonitrile, 10 parts of methyl methacrylate and 25 parts of styrene

3) Production of Thermoplastic Resin Compositions

The copolymer (A) and graft copolymer (B) produced as described above were mixed together in the latex form in a solids weight ratio of 75 : 25, and this mixed latex was, after adding an antioxidant, coagulated with calcium chloride, washed with water, filtered out and dried to obtain a powder composition (C).

Example 1

Sixty grams of the thus obtained mixed composition (C) of the copolymer (A) and the graft copolymer (B) and 40 g of polyvinyl chloride (Kanevinyl S-1001, produced by Kanegafuchi Chemical) together with 1 g of dioctyltin maleate, 1 g of dioctyltin mercaptide and 0.3 g of a low molecular weight polyethylene were kneaded on a roll mill heated to 185°C for 8 minutes. The sheet treated on the roll mill was pressed at 190°C and 100 kg/cm^2 for 15 minutes. The physical properties of the product are shown in Table 2.

As evident from Table 2, Examples C-1 to C-6 exhibit excellent mechanical properties, inter alia, high heat distortion temperature and impact strength. Those using the copolymers A-8, 9 and 10 respectively as the Comparative Examples are poor in heat resistance. That using A-8 shows significant coloration.

Table 2

	Example							Comparative Example			
	C-1	C-2	C-2'	C-3	C-4	C-5	C-6	C-8	C-9	C-9'	C-10
Copolymer (A)	A-1	A-2	A-2	A-3	A-4	A-5	A-6	A-8	A-9	A-9	A-10
Copolymer (B)	B-1	B-1	B-2	B-1	B-1	B-1	B-1	B-1	B-1	B-2	B-1
Izot Impact Strength *1 (kg·cm/cm)	23	40	41	44	41	37	43	47	43	41	39
Tensile Strength *2 (kg/cm^2)	543	535	537	533	538	533	531	535	541	536	535
Heat Distortion Temp.*3 (°C)	96	94	94	94	93	93	93	89	90	91	90
State of Coloration *4	No	No	No	No	No	No	No	Yellow	Yellow	No	No

*1 ASTM D-256

*2 ASTM D-636

*3 ASTM D-648

*4 Judged with the naked eye; "No" means no coloration

Example 2

Similarly as in Example 1, the composition according to the Example C1 and polyvinyl chloride resin, both in various amounts as indicated in Table 3, were mixed and treated together with 1 g of dioctyltin maleat, 1 g of dioctyltin mercaptide and 0.3 g of a low molecular weight polyethylene to obtain various compositions, whose properties were measured.

From these results it can be seen that the compositions of this invention (C-23 to C-28)are excellent both in impact strength and in heat resistance.

Table 3

	Comparative Example		Example						Comparative Example
	C-21	C-22	C-23	C-24	C-25	C-26	C-27	C-28	C-29
Copolymer Composition C-2 (pts)	0	20	30	40	50	60	70	80	100
Polyvinyl Chloride Resin (pts)	100	80	70	60	50	40	30	20	0
Izot Impact Strength (kg·cm/cm)	3	7	12	21	41	40	37	32	14
Tensile Strength (kg/cm^2)	560	554	551	547	541	535	532	526	521
Heat Distortion Temp. (°C)	75	79	82	86	89	94	98	103	114

Example 3

Sixty grams of each of mixtures of the copolymers (A) and (B) mixed in various ratios indicated in Table 4 and 40 g of polyvinyl chloride resin were processed similarly as in Example 1 to prepare test specimens.

As can be seen from the values of the physical properties, Examples D-2 to D-5 in which the mixing ratios of the copolymers (A) and (B) are in the range established by this invention have high heat distortion temperature and impact strength. Where too much of the graft copolymer (B) is present, the heat distortion temperature cannot be improved effectively and also impact strength is reduced. On the other hand, in the range where the graft copolymer is less than 10 parts, it seems there is almost no impact strength.

Table 4

	Comp. Ex.	Example				Comp. Ex.
	D-1	D-2	D-3	D-4	D-5	D-6
Copolymer A-2 (pts)	40	50	60	75	90	100
Copolymer B-1 (pts)	60	50	40	25	10	0
Izot Impact Strength (kg·cm/cm)	52	54	61	40	12	2
Tensile Strength (kg/cm^2)	440	477	508	535	581	610
Heat Distortion Temp. (°C)	86	89	91	94	98	102

What is Claimed is:

1. A thermoplastic resin composition which comprises 20 - 70 parts by weight of a polyvinyl chloride resin and 80 - 30 parts by weight of a mixed composition of the following copolymers (A) and (B) in the following mixing ratio:

(A) 90 - 50% by weight of a copolymer which comprises 65 - 90 parts by weight of α-methylstyrene with 35 - 10 parts by weight of acrylonitrile and 0 - 5 parts by weight of at least one copolymerizable vinyl monomer and contains 30 parts by weight or more of a component having an α-methylstyrene content of 82% by weight or higher; and

(B) 10 - 50% by weight of a graft copolymer obtained by reacting 35 - 80% by weight of a conjugated diene rubber and 65 - 20% by weight of a monomer or monomers comprising an aromatic monovinyl compound, an unsaturated nitrile compound or an alkyl methacrylate.

European Patent Office

EUROPEAN SEARCH REPORT

0043512

Application number
EP 81 10 4934

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	US - A - 3 678 132 (MASATAKA) * Claims 1-3 * --	1
X	GB - A - 1 400 848 (BASF) * Claims 1-3, 5 * --	1
	FR - A - 2 345 485 (BAYER) * Claims 1-3 * ----	1

CLASSIFICATION OF THE APPLICATION (Int Cl.^{3})

C 08 L 27/06
C 08 L 25/16

TECHNICAL FIELDS SEARCHED (Int. Cl.^{3})

C 08 L 27/06
25/16
25/12

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family
corresponding document

✓ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	15-10-1981	BOLETTI

EPO Form 1503 1 06.78